OFFICE OF NAVAL RESEARCH

GRANT or CONTRACT: N00014-93-1-0772

R & T Code 313T006

Technical Report #19

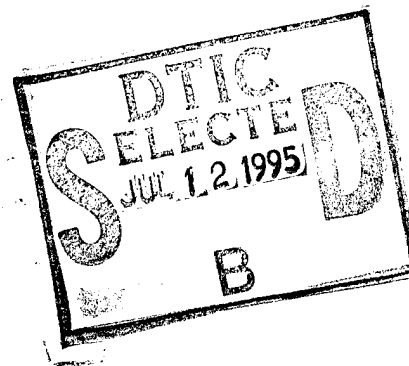Photochemistry and Photophysics of the Hydroxyfluorones and Xanthenes

Neckers, D.C. *Journal of Photochemistry and Photobiology* (invited) in press.

D. C. Neckers
Center for Photochemical Sciences
Dept. of Chemistry
Bowling Green State University
Bowling Green, OHIO 43402

· Date Submitted
June 15, 1995

DTIC
SELECTED
JUL 12 1995
B

19950705 076

DTIC QUALITY INSPECTED 8

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1 Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-188), Washington, DC 20503

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 6-15-95	3. REPORT TYPE AND DATES COVERED Technical Report

4. TITLE AND SUBTITLE

Photochemistry and Photophysics of the Hydroxyfluorones and Xanthenes

5. FUNDING NUMBERS

G N00014-93-J-1921
R & T 313T006

6. AUTHOR(S)

D.C. Neckers

Kenneth Wynne

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Center for Photochemical Sciences
Bowling Green State University
Bowling Green, Ohio   43402

8. PERFORMING ORGANIZATION REPORT NUMBER

19

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Department of the Navy
Office of Naval Research
800 North Quincy Street
Arlington, VA   22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Neckers, D.C. *Journal of Photochemistry and Photobiology* (invited) submitted.

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Reproduction in whole or in part is permitted for any
purpose of the United States Government. This document has
been approved for public release and sale; its distribution
is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

A review of the photophysics of electron transfer from tertiary aromatic amines and triarylalky borate anions to triplets formed from the xanthene dyes (Rose Bengal, Erythrosin, 6-acetoxy-9-(3,4,5,6-tetrachlorophenyl)-3-fluorone) and the hydroxyfluorones (2,4,5,7-tetraiodo-3-hydroxy-6-fluorone, 9-cyano-2,4,5,7-tetraiodo-3-hydroxy-6-fluorone, 2,4-diiodo-6-butoxy-3-fluorone). Invited in honor of the retirement of Professor Stefan Paszyc, Adam Mickiewich University, Poznan, Poland.

14. SUBJECT TERMS

15. NUMBER OF P

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF UL

Photochemistry and Photophysics of Hydroxyfluorones and Xanthenes

by

D. C. Neckers,[1] Salah Hassoon and Elena Klimtchuk

Center for Photochemical Sciences[2]
Bowling Green State University
Bowling Green, OHIO 43403

Laser initiated photopolymerization opened the doors for the rapid prototyping revolution. Driven by computer control, the polymerization process can create plastic models which conform accurately to a programmed design in three dimensions. The control programs may be derived from various sources including CAD files, CT scans or other tomographic medical imaging sources such as MRI in a process called 'stereolithography'. Models formed by stereolithography conform concisely to a design pattern in all dimensions, and the process has shortened the time required for implementation from months to days in industries ranging from automotive and glass to medical devices.

The Neckers program focuses on the processes of laser initiated photopolymerization and technologies thereby enabled.[3,4] The overall goal of the work is to understand the fundamentals of all steps of the complex processes from the light absorption and the disposition of the excited states formed initially through the sequence of reactions leading to solid photopolymer. An important technical goal is to relate the photophysics/photochemistry of the initiator system to the ultimate polymeric structure, and hence the physical, eventually mechanical, properties of the bulk polymer and/or shaped object, coating, or composite. A critical development in the evolution of the Neckers program was his relationship with Charles Hull, the inventor of the notion of rapid prototyping, and 3 D Systems where he, Neckers, was engaged as a consultant. Neckers and his students pioneered the use of stereolithography in medical imaging and in collaboration with Professor L. T. Andrews and his students[5] developed the first use of photopolymerization to convert CT and MRI data to three dimensional models for diagnosis and surgical planning.[6] An ultimate goal of the work is to form parts which can be used for complex machines or other devices, as contrasted to plastic models of parts, from a computer graphic generated by CAD, CT or MRI, by laser assisted photopolymerization.

A critical part of the basic program is to develop and understand new photochemistries for use with common commercial laser systems such as laser diodes. These sources are reliable, inexpensive and compact, and the photochemical systems which use them will be endowed with advantages in any application. To fulfill this goal we have undertaken the development of photopolymerization processes employing visible/infrared initiators. The majority of compounds absorbing visible radiation to produce the reactive intermediates responsible for initiation of reaction chains involved in polymerization do so by means of oxidation/reduction processes. Consequently a critical issue is study of electron transfer reactions of long wavelength absorbing dyes, most of which are bimolecular and require the presence of a partner reductant or oxidant called a coinitiator. Progress has been marked on the relationship of the photochemistry of the dye/coinitiator system to the mechanical properties of the polymers formed by the occurring chain reaction(s) and it is now possible to claim, with the developed systems, that photopolymerization initiated with visible light - with all of the advantages of that - supersedes photopolymerization with UV light in performance for selected applications. Since an important limitation of UV initiated polymerization is the inability to function in highly absorbing systems, or in systems filled with insoluble fillers such as those which provide structural reinforcement for plastic shapes, this technical achievement impacts particularly plans to develop methodology for the formation of engineering materials. Using laser initiated polymerization to make thin or thick films containing pigments of all colors has also now been achieved. We are also able to carry out polymerization in the presence of UV absorbers present in the system either adventitiously or purposely, e. g., as antioxidants. The latter are important to the long term photostability of polymeric coatings which are subject to light induced oxidative degradation.
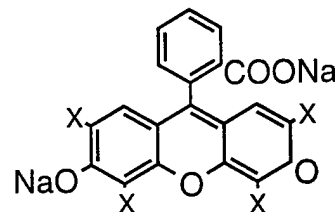
Our interest in visible light photoinitiators results from work on the development of the xanthene dyes, (X = H, halogen) both as singlet oxygen sensitizers and as photoinitiators.[7] We, and others, have specifically studied Eosin (X = Br) as a photoinitiator.[8] Eosin's spectral properties in polar solvents such as methanol (absorption; λ_{max} = 528 nm; ε_{max} = 1.1 x 10^5 M^{-1} cm^{-1}; emission; λ_{fl} = 547 nm $\emptyset_f$ = 0.59) are such that it is also almost perfectly suited as a potential initiating system for the argon ion laser (λ 514 nm). With electron donors such as triethylamine or triethanolamine it polymerizes acrylates when irradiated and it bleaches by means of known chemistry.[9,10] The mechanism involves reductive electron transfer to the dye
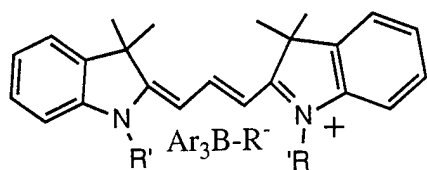
carbocyanine triarylalkyl borate

from the amine followed by proton loss from the triethanolamine radical cation (TEOA$^{+\cdot}$). The α-amino radical (TEOA$\cdot$) formed is the initiating radical.

Eosin/triethanolamine initiating systems also have certain limitations in three dimensional imaging applications[11]. Therefore as part of a program 'Photopolymerization in Three Dimensions' we sought better initiators by means of which to accurately control polymerization of a liquid monomer in all three dimensions x, y, and z relative to an initiating laser beam of some dimension striking an x,y monomer surface in the z direction, laser pulse of low power.

In a project designed to obtain infrared sources of singlet oxygen, Gottschalk turned to the cyanines which were known to absorb at much longer wavelengths than the commercial xanthenes[12]. Though the cyanines have limitations for this application, because triplet yields are very low in polar solvents, Gottschalk found other reactions. He invented the cyanine borate visible light photoinitiators in the mid-80's after just a few weeks on a project[13] intended to develop dyes which could be used as radical initiators at the wavelengths of the primary visible colors.[14]

The cyanine borates Gottschalk invented (R = alkyl, R' = alkyl) provided the basis for authentic color microcapsule color copying and printing based on the principles of "carbonless carbon paper" and developed into a color duplicating process eventually called Cycolor®.

The cyanine borates have generated intense interest mostly in the patent literature and mainly from Japan.[15] They give rapid photoresponse[16] in microcapsules filled with a polymerizable acrylate by producing radicals by extremely rapid electron transfer from the negative borate ion to the singlet state of the cyanine cation.[17] In triphenylalkyl borates, for example, this transfer is succeeded by loss of the alkyl radical from the oxidized borate, and formation of triphenylboron. The alkyl radical initiates polymerization. The cyanines have exceptionally high extinction coefficients, and this limits their use to applications such as imaging processes where incomplete conversion to polymer is an advantage. In the Cycolor process, an image is formed by breaking the microcapsules which contain dissolved acid sensitive, leuco dyes unto an acidic surface which usually resides on a second, partner surface called the developer layer. Photopolymerization incurred by the liquid monomers for the leuco

dyes contained in the microcapsules upon light absorption of the proper wavelength hardens that particular microcapsule and prevents the development of its contents upon rupture onto the acid surface.

Visible light photopolymerization, in general, offers many potential advantages over commercial UV systems. Visible sources remain simpler and easier to operate. A simple overhead projector can be used to demonstrate the use of visible polymerization systems. Relatively safe, more reliable, simpler (and less powerful) lasers are also available to produce longer wavelength light. As indicated above, most visible initiators function by electron transfer mechanisms (the light absorbing species is either oxidized or reduced in the excited state) and a number of them produce bleached products. Bleaching provides a greater depth of polymerization with the same irradiation dose.

Our first system post-xanthene was RBAX. On a general basis RBAX is a xanthone, analogous to the thioxanthones which are common commercial UV photoinitiators. The latter are used with typical tertiary amine accelerators and therefore can be described, as can benzophenone/Michler's ketone, as electron transfer UV photoinitiators. In other words the first step in the mechanism of their initiating polymerization is electron transfer from a donor - say a tertiary amine - to one or another thioxanthone excited state.
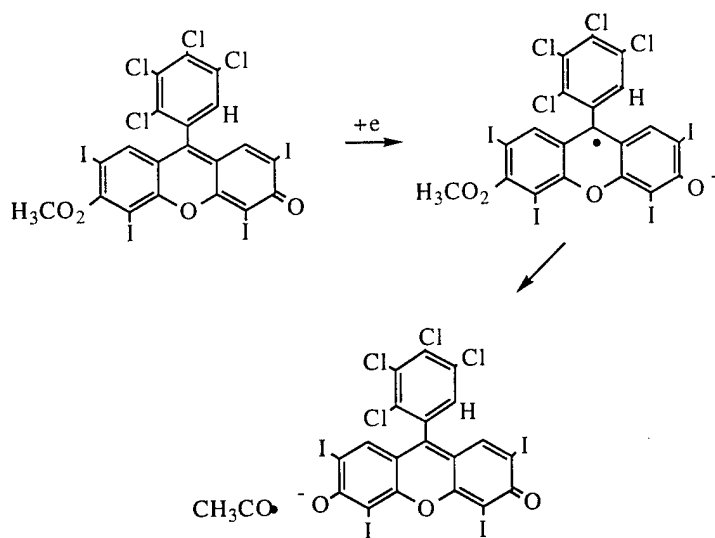

Based on the known photoreduction chemistry of Rose Bengal[18] we anticipated electron transfer would reduce the xanthene skeleton of RBAX and that the radical anion thence formed might decay by the elimination of an acetoyl radical. Acetoyl is analogous to benzoyl which is the radical which initiates chains in the case of most Norrish type I UV photoinitiators; i. e. benzoin ethers or acetophenone acetals. The proposed scheme is shown.

The spectral shape as well as the molar absorptivities of RBAX are similar to those reported for non-polar derivatives of Rose Bengal.[19] Irradiation of RBAX

(1.19 x 10^{-4} M) in the presence of triphenyl n-butyl borate ion (1.89 x 10^{-3} M) results in the bleaching of RBAX and the appearance of an absorption peak at 560 nm. This wavelength corresponds to λ_{max} for decarboxylated Rose Bengal (RB). Fluorescence measurements show that the excitation spectrum is identical with the absorption spectrum of decarboxylated RB. The bleaching products have not been isolated. Based on the known products for bleaching of Rose Bengal under reductive conditions and the fact that oxidation of triphenyl n-butyl borate ion generates butyl radical we expect the formation of the coupling product between RBAX and the butyl group. Therefore, the reaction can be represented as:

$$\text{RBAX} + \text{Bo}^- \xrightarrow{\quad h\nu \quad} \text{Bleaching product} + \text{RB} + \phi_3 B$$
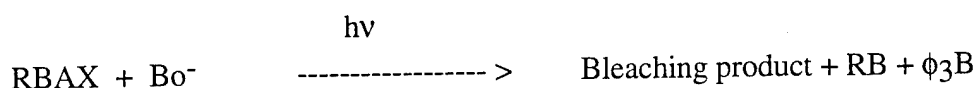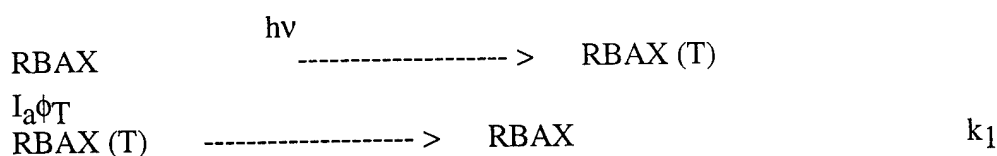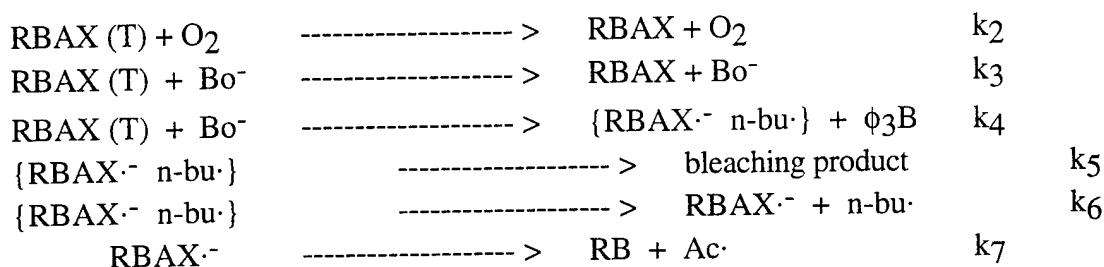
The quantum yields of RBAX bleaching and of RB generation were determined by measuring the decrease of the absorption at 486 nm and the increase in absorption at 560 nm as a function of light intensity and Bo$^-$ concentration. A summary of our results is as follows:

a) The rates of RBAX bleaching, -d [RBAX]/dt, and generation of decarboxylated Rose Bengal, d [RB]/dt, vary linearly with absorbed light intensity in the range between 1.0 x 10^{-5} and 1.2 x 10^{-4} einsteins/l x s.

b) ϕ (RB)/ϕ (-RBAX) is (8.6 $\pm$ 1.2) x 10^{-2}, independent of light intensity, Bo$^-$ concentration (1.0 - 24 mM) and the presence of air.

b) In argon-saturated solution and [Bo$^-$] = 1.89 x 10^{-3} M the quantum yield for bleaching of RBAX is 0.31.

The quantum yield of RBAX reduction is 0.39 $\pm$ 0.03 at infinite Bo$^-$ concentration. In view of the low Bo- concentrations required to observe the photoreduction we conclude that the reactive excited species is the triplet state of RBAX. Measurements of the lifetime of RBAX triplet by laser flash photolysis[20] yield values of 3.64 μs in argon-saturated solution and 288 ns in the presence of air. These lifetimes are independent of the energy of the laser pulse (0.2 - 3 mJ/pulse) and of the concentration of RBAX ground state in the range between 1.74 x 10^{-5} and 2.23 x 10^{-4} M.

A mechanism consistent with these observations is presented:

$$\text{RBAX} \xrightarrow{\quad h\nu \quad} \text{RBAX (T)} \qquad I_a \phi_T$$

$$\text{RBAX (T)} \xrightarrow{\quad\quad\quad} \text{RBAX} \qquad k_1$$

$$RBAX\ (T) + O_2\ \ ----------->\ \ RBAX + O_2 \qquad k_2$$

$$RBAX\ (T) + Bo^-\ \ ----------->\ \ RBAX + Bo^- \qquad k_3$$

$$RBAX\ (T)\ +\ Bo^-\ \ ----------->\ \ \{RBAX\cdot^-\ n\text{-}bu\cdot\}\ +\ \phi_3 B \qquad k_4$$

$$\{RBAX\cdot^-\ n\text{-}bu\cdot\}\ \ ----------->\ \ bleaching\ product \qquad k_5$$

$$\{RBAX\cdot^-\ n\text{-}bu\cdot\}\ \ ----------->\ \ RBAX\cdot^-\ +\ n\text{-}bu\cdot \qquad k_6$$

$$RBAX\cdot^-\ \ ----------->\ \ RB\ +\ Ac\cdot \qquad k_7$$

where n-bu· and Ac· represent n-butyl and acetyl radicals respectively. From laser flash photolysis measurements we obtain $k_1 = 2.78 \times 10^5\ s^{-1}$ and $k_1 + k_2\ [O_2] = 3.47 \times 10^6\ s^{-1}$ in air. The quantum yields are given by:

$$\phi(-RBAX) = \phi_T k_4\ [Bo^-]/(k_1 + k_2[O_2] + (k_3 + k_4)[Bo^-])$$

$$\phi(RB) = (k_5/k_5 + k_6)\phi(-RBAX)$$

The observation that the rate of RB generation varies linearly with the absorbed light intensity is evidence that the radicals $RBAX\cdot^-$ and n-bu· do not undergo significant recombination after dissociation of the geminate pair. Similarly the independence of $\phi(RB)/\phi(-RBAX)$ on the presence of air indicates that $RBAX\cdot^-$ is not significantly quenched by oxygen during the lifetime of the radical. The evidence for the lack of oxygen quenching of the geminate pair is presented below. Assuming that oxidation of $RBAX\cdot^-$ by oxygen is diffusion-controlled we obtain a minimum value for k_7 of $4 \times 10^8\ s^{-1}$.

The ratio $\phi(RB)/\phi(-RBAX)$ is equal to $(8.6 \pm 1.2) \times 10^{-2}$. From this value we derive $k_5/k_6 = 10.6 \pm 1.6$. We identify:

$$A = \phi_T k_4/(k_3 + k_4) = 0.39 \pm 0.03$$

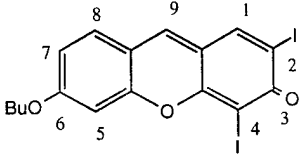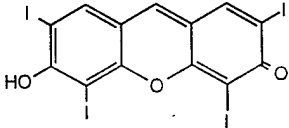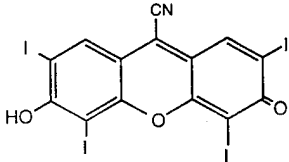$$B = (k_1 + k_2[O_2])/(k_3 + k_4) = (4.16 \pm 0.21) \times 10^{-3}\ M$$

by introducing the lifetime of RBAX triplet in the presence of air we derive $k_3 + k_4 = (8.35 \pm 0.42) \times 10^8\ M^{-1}\ s^{-1}$. Table I presents a summary of the different parameters we have derived from the mechanism along with the rate constants measured by laser flash photolysis.

In argon-saturated solution and for $[Bo^-] = 1.89 \times 10^{-3}\ M$ the quantum yield for consumption of RBAX is 0.31. From this value we calculate $\phi_T k_4/(k_3 + k_4) = 0.37$ in argon-saturated solution and conclude that the geminate pair (see Scheme I) does not react with oxygen, as deactivation of the geminate pair will affect the photoreduction quantum yield at infinite borate concentration.

Though both xanthenes and the cyanine borates have extensive histories, the advantages of visible light polymerization are not optimized by either group of

compounds. Xanthenes have serious solubility problems in most organic monomers. Cyanine borates offer a wide range of colors and are exceptional for photographic applications, but often produce poly(polyolacrylate) of low mechanical strength. They tend to remain deeply colored after polymerization thus precluding use in many situations. RBAX gave us a pattern to follow, but it had a number of problems which needed to be optimized, and we were really interested in longer wavelength absorbers. In order to broaden the versatility of visible initiators for applications where polymer properties are a major issue, *we developed a new series of initiators, the fluorones, and found conditions where they would form polymers of properties comparable to those formed with commercial UV initiator systems.* Photoreduction and photooxidation reactions of the fluorones can be used to initiate polymerization, depending on the coinitiator partner. In the presence of appropriate electron donors, such as tertiary amines, fluorones are reduced in a bimolecular electron transfer reaction. Electron transfer from the amine to the excited triplet state of the dye forms the dye anion radical and the amino cation radical. The latter rapidly releases a proton which transfers to the anion radical yielding a neutral dye and amino radicals the latter of which initiate free radical polymerization.[21] This is a critical achievement of the work. Approximately 35 new dyes in the basic fluorone series were synthesized to accomplish this objective.[22] Fluorones differ from the xanthenes by the absence of an aromatic group at C-9 (Table 1). This minor structural difference has important implications on the efficiency of the electron transfer, and subsequent, chemistry as well as on many other chemical properties. This substitution pattern also offers the flexibility of additional substitution at the 9-position on the ring system (Table 1).

Table 1: Properties of Example Fluorones

	DIBF	TIHF	TIHCF
λmax nm (ε) [1]	470 (30200)	536 (92600)	638 (80000)
λfl nm (τ ns); ϕ	broad (--); 0.02	548 (0.65); .13	654 (0.69); .02
λph nm (77°); ϕ	570	676 (0.87)	777 (0.99)
E(D-/D) v[2]	-.90	-.99	-.57
E(D/D+) v	1.40	1.34	–
red.; kq.m^{-1}s^{-1} [3]	1.2x10^8 (a)	2.4x10^7	8.9x10^8
	6.7x10^7 (b)		
ox.;kq.m^{-1}s^{-1} [4]	-0-	≈7x10^7	–
Air; kq.m^{-1}s^{-1}	2.5x10^9		

1) EtOH 2) vs. SCE
3) [dye] = 10^{-5} M; [ArNR$_2$] = 10^{-3}M; (a) ArNR$_2$ (b) Ar$_3$BR-: R = Alkyl; Ar = Ph
4) [dye] = 10^{-5} M; [Ar$_2$I$^+$, SbF$_6^-$] = 10^{-3}M

By virtue of this, groups which enhance the delocalization of charge over the aromatic skeleton yield fluorones whose absorption maxima are shifted substantially toward the red. The observation by Shi[10] that the fluorones bleach much more rapidly than do the xanthenes in the presence of agents which reduce their excited states, and that they form strong photopolymers much more rapidly in standard acrylate systems than do any related visible initiator compositions, led to an even greater interest in their chemistry. Fluorone bleaching is the result of the neutralization of the anionic, phenolic site produced by photoreduction of the dye triplet by cations produced upon oxidation of a partner electron transfer donor, and this enhances the properties of the polymer in most cases. For example it is productive in subsequent polymer forming steps, rather than detrimental as is the case with bleaching of comparable cyanines. The fluorones[23], when reduced by dialkylanilines, give two products (1).


$$R = alkyl, R' = H, ArN(CH_3)CH_2- \qquad (1)$$
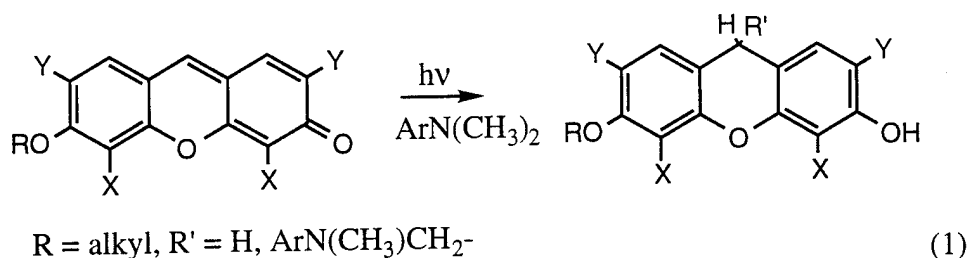
We have concentrated mechanistic studies on three fluorone dyes each of which targets a line of a common commercial laser.[24,25] Critical spectroscopic parameters and quenching constants measured by flash spectroscopy are assembled in Table 1.[26] Excitation of each dye, 2,4-diodo-6-butoxy-3-fluorone (DIBF), 2,4,5,7-tetraiodo-6-hydroxy-3-fluorone (TIHF) 9-cyano-2,4,5,7-tetraiodo-6-hydroxy-3-fluorone (TIHCF) gives, after intersystem crossing, high yields of triplets. The triplets, in turn, react with either amines or borate anions to give radicals which initiate polymerization with high efficiency. There is no evidence that DIBF triplets react with oxidizing agents such as diphenyliodonium hexafluoroantimonate, $\phi 2I+,SbF6-$ but those of TIHF and TIHCF do.

The flash photolysis results confirm that the photoreduction of (DIBF) in the presence of electron donor, tertiary amine (DIDMA) or borate salts (BORATE), is a one electron transfer process as shown in Scheme III and IV. An electron transfer from the borate anion or from the amine results initially in the DIBF radical anion (DIBF·-) and the boranyl radical pair in the first case and DIBF·- and the amino radical cation pair in the second. The transient spectra in the BORATE case show that DIBF·- is the only product obtained after quenching of the DIBF triplet. The formation of the radical anion was observed in the nanosecond time scale and in the same rate as the triplet decay rate.

This information proves that the cage escape to give free radicals (kd, scheme III) in this system is very fast and occurs on a shorter time scale. Schuster and coworkers[27] reported that in the cyanine-borate system, the boranyl radical dissociation to give triphenylborane and alkyl radicals is faster than the back electron transfer, that it depends on the stability of the alkyl radical formed and that the dissociation is irreversible. For the cyanine-triphenylbutylborate case they found that dissociation of the boranyl radical is very efficient or in other words the back electron transfer is not significant. In our system, where the electron transfer process is intermolecular, one should expect that the back electron transfer would be even less significant. In fact, the transient absorption and kinetic data obtained show that this was the case. The radical anion decay did not regenerate the dye as should be the case if back electron transfer occurs. Assuming that $k_{-et}=0$ (scheme III), and based on the observation that the rate of radical formation is the same as the rate of triplet decay, we estimate the electron transfer rate in this system to be as the measured triplet quenching rate which is 6.71×10^7 sec-1 This result is in good agreement with the values obtained in the previous work[26] with dye-amine systems, but it is very low compared to the intramolecular electron transfer rate ($k_{et}@10^{11}$ sec-1) obtained for the cyanine-borate systems.

Scheme III: Proposed mechanism in the case of DIBF and the BORATE:
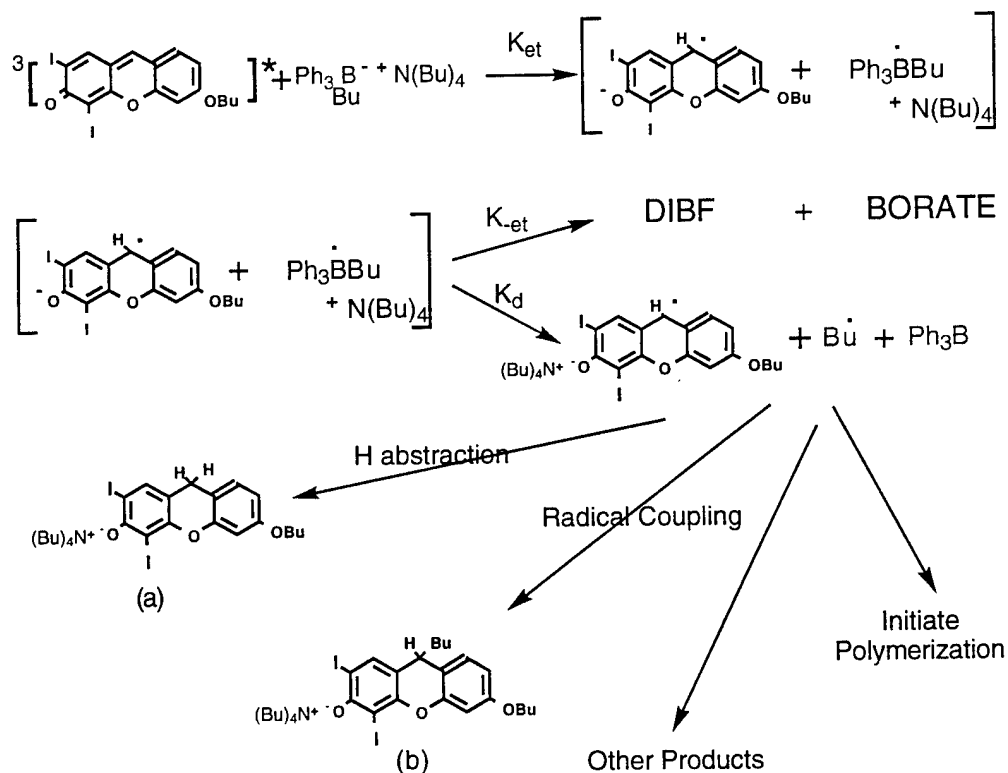
In the DIBF-DIDMA case, we were not able to see the dye radical anion in the nanosecond time scale. Instead the neutral dye radical (DIBF·) was obtained. Scheme IV describes the proposed mechanism in the present case. After the initial electron transfer from the amine nitrogen to the dye triplet, the DIBF·⁻ and amino cation radical pair is obtained. The dye radical anion has an oxygen radical center at the six position, which promotes a rapid proton transfer from the carbon a to the nitrogen in the amino cation radical[28], to give the neutral dye radical and the amine radical. In the presence of monomer, it was found that the amine radical and to some extent the dye radical, initiate polymerization. The protonation of the dye radical anion can happen inside or outside the solvent cage as shown in the scheme. In either way it is too fast (large k_{H+} and K_d) to measure on the nanosecond time scale. Also in this case the radical formation rate was the same as the rate of dye triplet decay and the radical decay did not regenerate the dye. Therefore, and similar to the BORATE case, we estimate the electron transfer rate to be as the triplet quenching rate, 1.21×10^8 sec^{-1}. This rate is 1.8 times faster than in the BORATE case and it is 5 times faster than in the similar system previously studied (TIHF-amine).

The free energy change DG_{et} for the electron transfer process calculated using the Rehm-Weller[29] equation (2), where $E_{ox}(D/D.+)$ is the oxidation potential of the electron donor

$$DG_{et} = E_{ox}(D/D.+) - E_{red}(A.-/A) - E^T_{0-0} - Ze^2/ea \qquad (2)$$

(DIDMA or BORATE), $E_{red}(A.-/A)$ is the reduction potential of the electron acceptor (DIBF) and E^T_{0-0} is the triplet excitation energy correlate very well with the obtained electron transfer rates. Ze^2/ea is the Coulombic energy, which is the free energy gained by bringing the two radical ions to an encounter distance a in a solvent with dielectric constant e. The reduction potential of DIBF measured by square-wave voltammetry [30] in acetonitrile is -0.9 V (vs SCE). The triplet excitation energy determined from the phosphorescence spectra is 2.3 eV. The literature reported oxidation potentials for similar borates66 and amines30 are ~ +0.7 V and ~ +0.5 V respectively. Assuming that the coulombic energy is too small, the calculated DG_{et} values are -0.7 eV for the BORATE case and -0.9 eV for the DIDMA case, compared to -0.36 eV, the reported result for TIHF-amine from the previous work[26].

Scheme IV: Proposed mechanism in the case of DIBF and DIDMA
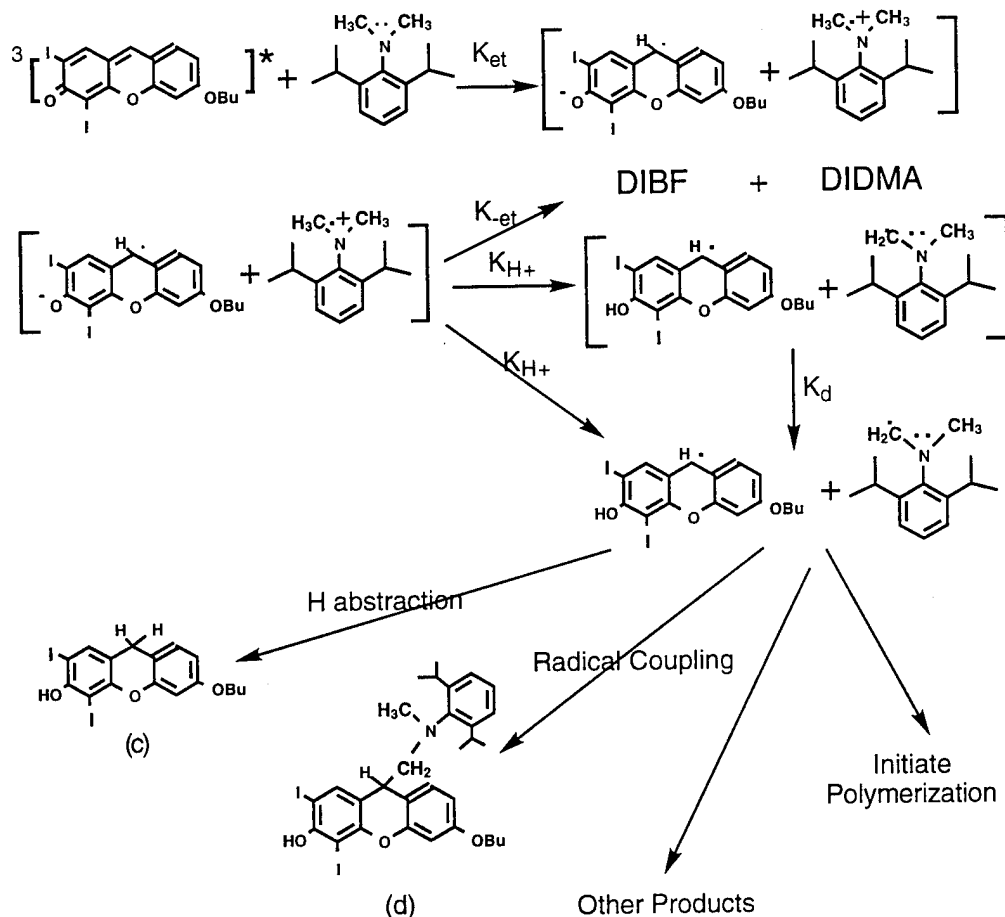
Scheme II

The fate of the radical anion DIBF·⁻ formed in the BORATE case and the neutral radical DIBF· formed in the DIDMA case determines the final bleached products observed in both systems. This has a major effect on the color of the formed solution. It was found that in the DIBF-DIDMA solution, after the solution was bleached by steady state irradiation, there is a relatively fast recovery of DIBF color (absorption). However, almost no recovery was found in the DIBF-BORATE solution. When OPPI was added to the solutions, color recovery obtained in the BORATE case also.

Analysis of the HPLC results of the bleached products support the mechanisms proposed. In the BORATE case, the ammonium cation (the counter ion of the borate salt) neutralizes the oxygen at the six position in the dye radical anion giving an ammonium "salt" radical, which abstracts a hydrogen atom from the solvent or couples to the butyl radical to give the reduced quinomethine ammonium salts (a) and (b). In a similar way, the neutral radical in the DIDMA case can give the quinomethines (c) and (d).

After irradiation of DIBF + DIDMA , three bleached products were obtained. One of these (Bleached 1) was confirmed to be the dihydro reduced form (c) as proposed in Scheme IV. The dihydro derivative (c) was obtained by reducing DIBF chemically (3):
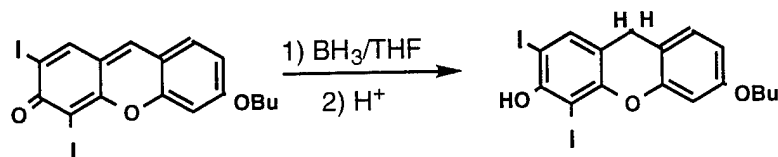
The bleached products 1 and 2 decreased after 72 hours while the concentration of DIBF recovered. If 1 is the dihydro derivative probably 2 would be the cross-coupled product (d). Phillips and Read[31] reported that in the photoreduction of eosin analog by tribenzylamine, 52% yield of the dihydro derivative and 39% yield of the cross-coupling product were obtained. In our case it seems that the cross-coupled bleached product is the principal product. However, and in agreement with Phillips and Read, we also observe that the cross-coupled product (d) is the one oxidized mainly reforming the initiator.

Comparing between the two cases, DIBF+DIDMA and DIBF+BORATE, after irradiation shows that in the case of the BORATE, no peaks were detected at higher rt range. However, the BORATE peak decreased and peaks with the same rt were observed at longer wavelengths. The UV-VIS absorption spectra of the new peaks are very similar to the absorption spectra of the anionic form of DIBF which also suggest that this forms has an ionic (salt) structure as proposed in Scheme III.

Small amounts of phenol and biphenyl obtained after irradiation in the borate case are probably a result of the reaction of oxygen with triphenylborane,[32] as biphenyl and phenol are found in larger amounts in the mixture than is triphenylborane.

Reoxidation of the quinomethine reduced products (a), (b), (c) and (d) will regenerate the original dye resulting in a colored solution, and depends in the polarity of the medium. In acetonitrile solution and in most of the photopolymer formulations it was observed that color recovery is fast when (c) and (d) are the reduced products but it is very slow from (a) and (b). This is reasonable where the reoxidation/deprotonation would be easier from the quinomethine (c) and (d) compared to the ammonium salts under (a) and (b) at the same conditions.

Conclusions:

Photoreduction of the xanthenes, the modified xanthenes and the fluorones leads to radicals when both aromatic amines and triarylalkyl borate salts are used as reducing agents. Triplet quenching is the primary pathway which converts dye excited states to radical anions. Oxidation of the partner produces radicals by a series of routes.

Mechanistic details and product study results have been reported.

References:

1 This publication summarizes the work of several post-doctorals and research associates. It is a pleasure to acknowledge the work of Oscar Valdes-Aguilera, Jianmin Shi, and Darrell Watson. They did most of the work described herein. The senior author is delighted to acknowledge their outstanding contributions. The work has mostly been published in detail elsewhere. The reader is referred to the references which follow for the original citations.
2 Contribution #236 from the Center for Photochemical Sciences.
3 Hull, C. U. S. Patent, 4, 575, 330 March 11, 1986
4 Neckers, D. C., *Spectrum*, Vol 2, (1990) 4, 1 ; *Chem Tech,*, 20, (1990) 615; *Polymer Science and Engineering, 32* (1992) 1481.
5 Director of Imaging Analysis Laboratory, Medical College of Ohio, Toledo, OHIO
6 Neckers, D. C., patent disclosure, Arnold, White and Durkee, March 1, 1987; Neckers, D. C., Valdes-Aguilera, O,, Andrews, L. T. and Cubit, T., unpublished results; October 17, 1987.
7 Neckers, D. C.; Linden, S.M. *J. Am. Chem. Soc., 110* (1992) 1257; Neckers, D. C.; Valdes-Aguilera, O. *Accounts of Chemical Research,* 22 (1989) 171; Valdes-Aguilera, O.; Neckers, D. C., *Advances in Photochemistry,* Vol 18, Volman, D., Hammond, G. S. and Neckers, D. C., ed; Wiley, NY, 1993, p 341 ff.
8 The interested reader is referred to some of these recent reviews. See, for example, O. Valdes-Aguilera and D. C. Neckers, *Accounts of Chemical Research, 22* (1989) 171 ; D. C. Neckers, *J. Chem. Ed., 64* (1987) 649 . D. C. Neckers, *J. Photochem. Photobio., 44* (1989) 1 .
9 A. Zakrewski and D. C. Neckers, Tetrahedron, *Tetrahedron, 43* (1987) 4507 ; and references cited therein.
10 Neckers, D.C.; Raghuveer, K.S. and Valdes-Aguilera, O. *Polym. Materials Sci. Eng. 60* (1989) 15 .
11. Neckers, D.C., unpublished.
12 Gottschalk, P.; Erickson, J.; Neckers, D. C. *J. Photochem. & Photobiol., 43* (1986) 379;
13 Gottschalk, P., Neckers, D. C. and Schuster, G. B., U. S. Patent, 4,772, 530, Sept. 20, 1988, Gottschalk, P., Neckers, D. C., Schuster, G. B., Adair, P. C., and

Pappas, S. P., U. S. Patent, 4,937,159, June 26, 1990; Neckers, D. C. and Linden, S. M U. S. 4,924,009; January 10, 1990.

14 This is a classic case of so-called 'indirect' technology transfer. Gottschalk, working on cyanines with the PI, found an interest in borate anions at Mead Imaging as a result of a consulting relationship Mead had at the time with Gary B. Schuster. Gottschalk's contribution was to recognize that the potential of the ion pair, Cy+, Borate-.

15 Typical recent patents: Yamaguchi, J; Okazaki, M., Jpn Kokai Tokkyo Koho, CA 112:28152 (1990); Yamaguchi, J., Shinozaki, F., Ishage, S., Adachi, K., Okazaki, M. Jpn. Kokai Tokkyo Koho, 01 72,150; CA 112 28150 d, (1990); Paatel, R. C., Thien, T. V., Warner, D., Eup. Pat. Appl. EP 444,786 (1991); Washisu, S., Jpn 02,205, 851; CA, 114, 91988f (1991); Kawamuro, K.; Okamoto, Y., Ger. Offen DE 3,834,960; CA 111, 222173 h (1989); Kondo; K. Murofushi, K., Gan, G., Hosada, K. Jpn Kokai Tokkyo Koho JO 04,261,406; CA 118 213733, h (1994).

16 Fast photoresponse means different things to different groups. Our goal is < 1mJ/cm2 at a single wavelength; I. e., with a laser radiation source.

17 Yang, X,; Zaitsev, A.; Sauerwein, B; Murphy, S; Schuster, G. B. *J. Amer. Chem. Soc.* , *114* 7 (1992) 93 *et. seq.*

18 See, for example, O. Valdes-Aguilera and D. C. Neckers, *Accounts of Chemical Research, 22* (1989) 171 ; D. C. Neckers, *J. Chem. Ed., 64* (1987) 649 . D. C. Neckers, *J. Photochem. Photobio., 44* (1989) 1 . D. C. Neckers and O. M. Valdes-Aguilera, *Advances in Photochemistry, 315* (1993).

19 See, for example, Lamberts, J. J. M., Schumacher, D. R. and Neckers, D. C. *J. Am. Chem. Soc., 106* (1984) 5879 ;J. Paczkowski, J. J. M. Lamberts , B. Paczkowska, and D. C. Neckers, *J. Free Radicals in Biology & Medicine, 1* (1985) 341. D. Xu, A. VanLoon, S. M. Linden, and D. C. Neckers, *J. Photochem., 38* (1987) 357 .

20 The triplet of RBAX is monitored at 610 nm. We will report our complete flash photolysis study in a future publication.

21 For a review of the xanthenes in photopolymerization see Valdes-Aguilera, O. and Neckers, D.C., *Advances in Photochemistry*; Volman, D.H., Hammond, G.S., Neckers, D.C., Eds.; Wiley, NY, 1993, Vol. 18., pp 313-394.

22 Valdes-Aguilera, O.; Pathak, C.P.; Shi, J.; Watson, D.; Neckers. D.C. *Macromolecules 25* (1992) 541; Shi, J.; Zhang, X-P.; Neckers, D. C., *Tet. Letters, 34* (1993) 6013; Shi, J.; Zhang, X-P.; Neckers, D. C. *J. Org. Chem., 57* (1992) 4418; Liu, Q.; Neckers, D. C., unpublished.

23 Hassoon, S.; Neckers, D. C. *J. Phys. Chem., 99* (1995) xxxx.

24 Neckers, D. C. and Shi, J-M., U. S. Patent, 5,395,862, March 7, 1995.

25 The reasons for selection include solubility in a variety of monomer systems, electron transfer characteristics, bleaching rates, ease of use, ease of synthesis, stability when formulated in prepolymer mixtures, and so on. The laser lines targeted are the 488 and 514 nm lines of the Argon ion laser, and the 632 nm line of the He/Ne laser.

26 Klimtchuk, E.; Rodgers, M. A. J.; Neckers, D.C. *J. Phys. Chem., 96* (1992) 9817

27 Chatterjee, S.; Davis, P.D.; Gottschalk, P.; Kurz, M.E.; Sauerwein, B.; Yang, X. and Schuster, G.B. *J. Am. Chem. Soc. 112* (1990) 6329 and references therein.

28 a) Cohen, S.G., Pavola, A. and Parsons Jr., *Chem. Rev., 73* (1973) 141. b) Cohen, S.G., *J. Am. Chem. Soc., 102* (1980) 1419.

29 Rehm, D.; Weller, A. *Isr. J. Chem.* 8 (1970) 259.

30 Murov, S. L.; Carmichael, I.; Hug, G. L.; *Handbook of Photochemistry*, 2nd Ed., Marcel Dekker Inc., 1993, p. 289.

31 Phillips, K. and Read G., *J. Chem. Soc. Perkin Trans.* 1 (1986) 671.

32 Doty, J. C.; Grisdale, P. J.; Evans, T. R.; Williams, J. L. R. *J. Organometal. Chem.* 32 (1971) C35.